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(21) International Application Number: PCT/US98/08300 (22) International Filing Date: 24 April 1998 (24.04.98) (30) Priority Data: 08/840,045 24 April 1997 (24.04.97) US (71) Applicant: S. C. JOHNSON & SON, INC. [US/US]; 1525 Howe Street, Racine, WI 53403 (US). (72) Inventor: KLINKHAMMER, Michael, E.; 3510 – 21st Street, Racine, WI 53405 (US). (74) Agents: BOZEK, Laura, L. et al.; Patent Section, S.C. Johnson & Son, Inc., 1525 Howe Street, Racine, WI 53403 (US).		(81) Designated States: CA, MX. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: CHLORINATED IN-TANK TOILET CLEANSING BLOCK (57) Abstract Disclosed herein is a toilet cleansing block containing a chlorine releasing agent. A preferred block is formulated with a cellulose ether to prolong life, a dye, and a stabilizer to suppress adverse interactions between the chlorine releasing agent and the cellulose ether, as well as between the chlorine releasing agent and the dye.		

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CHLORINATED IN-TANK TOILET CLEANSING BLOCK

Technical Field

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The present invention relates to cleansing blocks suitable for immersion in toilet tanks. The blocks are formulated to inhibit formation of toilet rings and surface stains.

10 Background Art

Various cleansing blocks for use in toilet tanks and other water reservoirs are known. Such cleansing blocks typically contain a surfactant for cleaning, and often fillers, binders, colorants, extrusion aids and perfumes. They are designed
15 to slowly release these materials into the toilet basin each time the toilet is flushed.

One particularly desirable form of such cleansing blocks are those that release chlorine compounds into the water supply to help clean and disinfect the toilet basin. See e.g. U.S. patent 5,336,427. However, chlorinated cleansing
20 blocks can have a relatively short usage life.

Creating longer life chlorinated cleansing blocks has been a significant challenge. Among other things, such cleansing blocks should not include materials which leave undesirable residues in the toilet bowl, which are environmentally unacceptable, which have unpleasant odors, or which have
25 incompatibility with other components. For example, cellulose ether binders are known to prolong the life of some toilet cleansing blocks. See e.g. U.S. patent 4,269,723. However, they can be unstable in the presence of chlorine releasing

compounds. Also, chlorine releasing agents can interfere with some dyes used in such blocks.

Thus, it can be seen that a need exists for an improved toilet chlorinated cleansing block.

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Disclosure Of Invention

In one aspect, the invention provides a water reservoir cleanser (e.g., in block form) having 1%-40% of a chlorine releasing agent selected from the group consisting of chloroisocyanurates, hypochlorites, chlorosuccinimides, chloramine T (sodium para-toluene sulfochlorine), and chlorodimethyl hydantoin; 1% to 20% cellulose ether binder; and at least 10% of a surfactant (preferably an anionic surfactant). There is also at least 2% of a stabilizer selected from the group consisting of mineral oil, isobornyl acetate, C₁₂ - C₂₀ linear alcohols, and
15 fragrance oils that have a specific gravity of less than 1 and are chlorine stable.

Examples of fragrance oils of this type are pine oil, Quest Q-7940A (Quest International Fragrances USA Inc. - herbal/pine), IFF Cloriffic 630 (International Flavors And Fragrances Inc. - lemon/citrus), and Takasago AG 4761-BHT (Takasago International Corporation - apple). It is especially preferred that such
20 fragrance oils have a specific gravity between .83 and .98 and be essentially insoluble in water. One especially preferred fragrance oil is Unipine 85, a pine oil from Bushe, Boake and Allen, Inc. This fragrance oil has the added advantage of facilitating extrusion of the blocks during manufacture.

A test which can be performed to determine if a fragrance is chlorine
25 stable is as follows. A small amount of solid chlorine containing compound is placed into a beaker. A sufficient amount of fragrance is added to substantially coat all of the particulate. The sample is observed periodically over a 24 hour period. The fragrance is considered stable as long as (1) there is no observable

chemical reaction (e.g., exothermic, combustion); (2) there is no detectable strong chlorine odor from the sample; (3) there is no discoloration of the sample; and (4) the fragrance's characteristic odor has not significantly changed.

To achieve long life a cellulose ether binder is included in the block.

5 Preferred cellulose ether binders are hydrated cellulose materials such as hydroxy alkyl celluloses such as hydroxy ethyl cellulose, hydroxypropyl methyl cellulose, and hydroxy propyl cellulose. Examples of other cellulose ether binders are methyl cellulose, ethyl cellulose, sodium carboxymethyl cellulose, ethyl hydroxyethyl cellulose, and carboxymethyl cellulose. It is believed that the
10 stabilizer reduces the hydrolyzing effect of the bleach on the cellulose ether binder.

For toilet cleaning blocks, anionic surfactants are especially preferred, such as sodium dodecyl benzene sulfonate and sodium lauryl sulfate. However, a wide variety of surfactants (anionic, nonionic, cationic, zwitterionic), are suitable
15 for use in toilet cleansing blocks (see e.g. 5,336,427).

Preferred chlorine releasing agents are alkali metal and alkaline earth metal hypochlorites, and alkali metal dichloroisocyanurates.

Surprisingly, even though the block has a bleach, the block can also include dye. In this regard, I have found that the stabilizer also reduces the
20 oxidizing effect of the bleach on the dye. The choice of the dye/coloring agent will largely depend on the color desired for the water into which the lavatory cleanser composition is to be dispensed and its tendency not to stain porcelain. A preferred coloring agent is Acid Blue 9. Other suitable dyes are described in U.S. patent 5,336,427.

25 The amount of coloring agent or dye to be dispensed into the water will depend on the color intensity desired and the cost of the dye. The absorbance of the coloring agent may be determined for laboratory purposes through the use of

a visible spectrophotometer, such as a Perkin-Elmer Model 552 spectrophotometer.

5 The amount of coloring agent delivered in the toilet bowl should be sufficient to provide an absorbance in a 1 cm spectrophotometric cell of from about 0.02 absorbance units ("a.u.") to about 0.2 a.u. when measured at its wavelength maxima. This is because consumers typically believe that a colored cleansing product is no longer working when it has a color intensity below this range.

Also, a filler/density aid, and various other conventional additives such as
10 borax or ascorbic acid can be included. For example, to achieve adequate density so that the block will not float, and to minimize costs, inert fillers/density aids are preferably added. Inert salts are preferred for this purpose such as water-soluble inorganic or organic salts (or mixtures of such salts). Examples include various alkali metal and/or alkaline earth metal sulfates, chlorides,
15 borates, and citrates. Specific inert salts are sodium sulfate, sodium sulfonate, calcium sulfate, sodium chloride, potassium sulfate, sodium carbonate, lithium chloride, tripotassium phosphate, sodium borate, potassium fluoride, calcium chloride, magnesium chloride, sodium citrate, magnesium sulfate and sodium fluoride. The filler/density aid is typically present in an amount from about 0% to
20 about 60%, preferably about 10% to about 40% by weight.

In another embodiment, the invention provides a method of cleaning a basin of a toilet. One immerses one of the above blocks in a water reservoir for a toilet basin, allows a portion of the block to dissolve in the toilet tank water, and then flushes the toilet.

25 The objects of the present invention therefore include providing a water reservoir cleaner of the above kind:

- (a) that is effective in inhibiting toilet bowl stain formation;
- (b) that maintains toilet basins in a clean condition for an extended period;

(c) that uses environmentally acceptable and inexpensive components;
and

(d) that compatibly uses a chlorine releasing agent for cleaning, a
cellulose ether for extended life, and a dye for providing an easy way for a
5 consumer to tell when a replacement is needed.

These and still other objects and advantages of the present invention
(e.g., methods for using these blocks) will be apparent from the description which
follows. The following description is merely of the preferred embodiments. Thus,
the claims should be looked to in order to understand the full scope of the
10 invention.

Modes for Carrying Out Invention

Cleansing blocks for use in a toilet tank are:

15 Example I - Control - No Stabilizer

<u>Ingredient</u>	<u>Weight %</u>
Sodium dichloroisocyanurate, 60% active	6%
Hydroxy ethyl cellulose	5%
Sodium dodecyl benzene sulfonate, 85% active (Ufaryl DL-85)	60%
Sodium sulfate	19%
Borax 5M	10%

Example II - Alcohol And Fragrance Oil

<u>Ingredient</u>	<u>Weight %</u>
Sodium dichloroisocyanurate, 60% active	6%
Hydroxy ethyl cellulose	5%
Sodium dodecyl benzene sulfonate, 85% active (Ufaryl DL-85)	60%
Neodol 23 (C ₁₂ /C ₁₃ linear primary alcohol)	3.5%
Borax	10%
Sodium sulfate	12%
Fragrance oil	3.5%

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Example III - Alcohol

<u>Ingredient</u>	<u>Weight %</u>
Sodium dichloroisocyanurate, 60% active	6%
Hydroxy ethyl cellulose	5%
Sodium dodecyl benzene sulfonate, 85% active (Ufaryl DL-85)	60%
Neodol 23 (C ₁₂ /C ₁₃ linear primary alcohol)	7%
Borax	10%
Sodium sulfate	12%

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Example IV - Fragrance Oil

<u>Ingredient</u>	<u>Weight %</u>
Sodium dichloroisocyanurate, 60% active	6%
Hydroxy ethyl cellulose	5%
Sodium dodecyl benzene sulfonate, 85% active (Ufaryl DL-85)	60%
Borax 5M	10%
Sodium sulfate	12%
Fragrance oil	7%

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Example V - Pine Oil and Dye

<u>Ingredient</u>	<u>Weight %</u>
Sodium dichloroisocyanurate, 60% active	6%
Hydroxy ethyl cellulose	5%
Sodium dodecyl benzene sulfonate, 85% active (Ufaryl DL-85)	60%
Acid Blue #9 dye	8%
Sodium sulfate	11%
Pine oil, Unipine 85	10%

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Example VI - High Chlorine Content

<u>Ingredient</u>	<u>Weight %</u>
Sodium dichloroisocyanurate, 60% active	27%
Hydroxy ethyl cellulose	3%
Sodium dodecyl benzene sulfonate, 85% active (Ufaryl DL-85)	60%
Pine oil, Unipine 85	10%

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In other preferred formulations, total surfactant is preferably between 40 and 80%, total cellulose ether is preferably between 1 and 20% (even more preferably between 5 and 15%), and the chlorine releasing agent is preferably
15 between 1 and 60% (even more preferably between 5 and 40%) of the block. Total stabilizer is preferably between 2 and 20% of the block, even more preferably between 4 and 12%. When a dye is used, it is preferably between 1 and 20% of the block (e. g. 10% of the block when Acid Blue #9 is used).

To make blocks of the present invention, we preferably first create a
20 homogeneous blend using a mixer such as a ribbon blender. The blend is then

fed into the barrel of a screw extruder and passed through the extruder to form a continuous extrudate which is then cut to the size block desired.

5 The pressure through the die can be about 500-1250 psi. The barrel of the extruder can be maintained at less than 35E C. (e.g., an ambient temperature) by means of cooling water circulated through an external barrel jacket. The die head may be heated to assure a smoother surface of the product extrudate.

10 The block in the continuous extrudate form begins to cure upon leaving the extruder, and hence can be cut into cleansing blocks of requisite size by conventional cutting means downstream of the die and before substantially complete curing. The "block" need not be rectangular. It may be a tablet, disk, brick, or other solid mass, with or without crevices, holes or the like, and need not be formed by extrusion (albeit extrusion is preferred). Thus, any solid form mass is intended to be a "block" for purposes of this patent.

15 To test the blocks of the present invention, we placed such blocks in a conventional Kohler 3.5 gallon toilet tank. We flushed the toilet periodically as per a protocol that represented the median consumer usage (10 flushes per day, no flushes between 11 PM and 8 AM, etc.). Periodically, we tested and inspected for whether any of the block remained in the toilet tank.

20

Results

As one example, using 50.1 g - 50.3 g blocks made from the Examples I (Control) and IV, the life of the blocks were as follows:

25 Example I - 7 days

Example IV - 35 days

Thus, the stabilizer greatly increased the useful life of the chlorinated block.

Industrial Applicability

The invention is useful in maintaining the cleanliness of toilet bowls associated with toilet tanks. It should also have applicability in other water reservoir systems (e.g. tanks for urinals).

CLAIMS

We claim:

1. A water reservoir cleaner, comprising:
1% to 60% by weight of chlorine releasing agent;
5 at least 2% by weight of stabilizer selected from the group
consisting of mineral oil, isobornyl acetate, C₁₂ - C₂₀ linear alcohols, and bleach
stable fragrance oils that have a specific gravity of less than 1;
1% to 20% by weight cellulose ether binder; and
at least 10% by weight of a surfactant.
10
2. The cleaner of claim 1, wherein the surfactant is an anionic
surfactant and the cleaner is in block form.
3. The cleaner of claim 1, wherein the surfactant is sodium dodecyl
15 benzene sulfonate.
4. The cleaner of claim 1, wherein the block further comprises a dye.
5. The cleaner of claim 1, wherein the chlorine releasing agent is
20 selected from the group consisting of chloroisocyanurates, hypochlorites,
chlorosuccinimides, sodium para-toluene sulfochlorine, and chlorodimethyl
hydantoins.
6. The cleaner of claim 1, wherein the cellulose ether binder is a
25 hydroxy alkyl cellulose.

7. A method of cleaning a basin of a toilet, comprising the steps of:
immersing a block of the claim 1 cleaner in a water reservoir for the toilet
basin;
dissolving a portion of the block in water in a toilet tank; and
5 flushing the toilet.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/08300

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D3/395 C11D3/18 C11D3/20 C11D3/50
C11D3/22

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 336 427 A (BUNCZK CHARLES J. ET AL.) 9 August 1994 cited in the application see column 3, line 50 - column 4, line 3 see claims 1-5; examples ---	1-5,7
A	US 4 269 723 A (BARFORD ERIC D. ET AL.) 26 May 1981 cited in the application see column 3, line 3 - column 4, line 58 see claims ---	1-7
A	W0 92 18605 A (JEYES LTD.) 29 October 1992 see page 1 - page 5 see page 8; claims; examples --- -/--	1-5,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 273 106 A (JEYES GROUP PLC.) 8 June 1994 see page 1 - page 5 see claims; examples ---	1-5,7
A	US 4 722 802 A (HUTCHINGS R. S. ET AL.) 2 February 1988 see claims 39-59 ---	1-4,6,7
A	EP 0 537 025 A (STAFFORD-MILLER LTD.) 14 April 1993 see claims; examples ---	1,6
A	EP 0 018 679 A (THE PROCTER & GAMBLE CO.) 12 November 1980 see page 1 - page 4 see page 15 - page 18 see claims ---	1-5,7
A	EP 0 462 643 A (UNILEVER NV.) 27 December 1991 see the whole document ---	1-5,7
P,A	WO 97 44435 A (S.C. JOHNSON & SON INC.) 27 November 1997 see the whole document -----	1-4,6,7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5336427 A	09-08-1994	US 5205955 A US 5449473 A AU 652836 B AU 1839892 A CA 2071017 A EP 0526437 A JP 5186799 A	27-04-1993 12-09-1995 08-09-1994 07-01-1993 04-01-1993 03-02-1993 27-07-1993
US 4269723 A	26-05-1981	AU 533241 B AU 4538379 A BE 874982 A BR 7901749 A CA 1125620 A CH 643882 A DE 2910955 A FR 2420570 A NL 7902174 A ZA 7901355 A	10-11-1983 27-09-1979 16-07-1979 20-11-1979 15-06-1982 29-06-1984 04-10-1979 19-10-1979 25-09-1979 28-05-1980
WO 9218605 A	29-10-1992	AT 128181 T AU 667039 B AU 1982192 A BR 9205926 A CA 2108975 A DE 69204997 D DE 69204997 T DK 581826 T EP 0581826 A ES 2080497 T GB 2270084 A, B GR 3017997 T HK 177395 A JP 6506711 T MX 9201849 A NZ 242448 A	15-10-1995 07-03-1996 17-11-1992 05-07-1994 23-10-1992 26-10-1995 11-04-1996 08-01-1996 09-02-1994 01-02-1996 02-03-1994 29-02-1996 01-12-1995 28-07-1994 01-10-1992 27-04-1994
GB 2273106 A	08-06-1994	AT 157699 T AU 678416 B AU 5431594 A CA 2150458 A	15-09-1997 29-05-1997 22-06-1994 09-06-1994

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2273106 A		DE 69313663 D EP 0672103 A ES 2110634 T WO 9412612 A GB 2288814 A ZA 9308634 A	09-10-1997 20-09-1995 16-02-1998 09-06-1994 01-11-1995 01-08-1994
US 4722802 A	02-02-1988	AU 595015 B AU 7047387 A CA 1282295 A	22-03-1990 01-10-1987 02-04-1991
EP 0537025 A	14-04-1993	CA 2080396 A US 5188755 A AU 649569 B AU 2633192 A JP 6116597 A NZ 244677 A AT 156856 T DE 69221572 D DE 69221572 T DK 537025 T ES 2104844 T MX 9205832 A	14-04-1994 23-02-1993 26-05-1994 22-04-1993 26-04-1994 27-06-1994 15-08-1997 18-09-1997 18-12-1997 01-09-1997 16-10-1997 01-04-1993
EP 0018679 A	12-11-1980	US 4246129 A CA 1139633 A JP 56004699 A	20-01-1981 18-01-1983 19-01-1981
EP 0462643 A	27-12-1991	AU 628749 B AU 7838691 A CA 2044490 A,C DE 69104780 D DE 69104780 T ES 2063436 T JP 2042644 C JP 4252300 A JP 7065080 B	17-09-1992 19-12-1991 19-12-1991 01-12-1994 02-03-1995 01-01-1995 09-04-1996 08-09-1992 12-07-1995
WO 9744435 A	27-11-1997	AU 3205197 A	09-12-1997